

RADIATION TREATED ETHYLENE POLYMERS AND ARTICLES MADE FROM SAID POLYMERS

1.0 RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Patent Application _____ (Docket No. 33702/US), entitled "Method of Increasing The Hydrostatic Stress Strength Of A Polymer," filed October 17, 2003, which is the national stage of PCT Application No. PCT/ZA03/00053, of the same title, filed April 17, 2003, which designates the United States and claims priority to South African Application No. ZA 2002/3121, filed April 19, 2002. The entire content of the aforementioned documents is incorporated by reference.

2.0 BACKGROUND OF THE INVENTION

2.1 Field Of The Invention

The invention relates to irradiated ethylene polymers and articles made using said polymers. More specifically, the invention relates to ethylene polymers that are modified by ionizing radiation, in air, at a temperature less than the crystalline melt temperature of the polymer, prior to article formation, as well as articles made from said polymers.

2.2 Related Art

Polyethylene is one of the most widely used commercial synthetic thermoplastic polymers. Polyethylene is inexpensive, easy to process and convert into articles, tough and flexible. In addition, polyethylene is a good electrical insulator over many frequencies. Polyethylene also exhibits better chemical resistance, including moisture stability, than other commercial plastics including nylon. Furthermore, thin films of certain grades of polyethylene are transparent. Polyethylene also exhibits excellent physiological compatability characteristics.

The commercial importance of polyethylene is enhanced by the wide variety of grades that exist, each having different physical properties and, therefore, different end-use applications. Polyethylene can be coated onto, or formed into, a wide variety of products using conventional conversion technologies such as extrusion, injection molding, cast molding, film and bottle blowing and powder coating.

Despite its popularity, polyethylene has several shortcomings. For example, polyethylene has relatively low mechanical properties (e.g., tensile strength, impact strength,

1 flexural modulus, hydrostatic stress strength, etc.), poor environmental stress crack resistance
2 (ESCR), low service temperature, and relatively poor adhesion to polar surfaces.

3 Crosslinking polyethylene is well known. For example, it is known to crosslink
4 polyethylene with chemicals, *e.g.*, peroxides, silane and/or multi-functional (meth) acrylates.
5 Alternatively, it is known to crosslink polyethylene with ionizing radiation, *e.g.*, using
6 electron beam or gamma radiation.

7 Irradiating artifacts formed from polyethylene to improve mechanical properties and
8 thermal stability is known. Such artifacts include polyethylene coated cables and wires,
9 underfloor hot water piping, heat shrinkable polyethylene films, and polyethylene foams,
10 gaskets and o-rings. Generally, a high degree of crosslinking (*e.g.*, 60-70% gel content) is
11 imparted by such processes.

12 However, there has been little research and development on, and much less
13 commercialization of, polyethylene resins crosslinked by ionizing radiation prior to artifact
14 formation. One reason for this lack of research is the understanding that high levels of
15 crosslinking drastically decreases melt flow, making the polymer difficult to process and
16 convert into artifacts. To the extent that irradiated ethylene polymers are discussed in the
17 prior art, the irradiation of the polymer is generally done under non-ambient atmosphere
18 and/or above the crystalline melt temperature and steps are generally taken to insure an
19 extremely low gel content (*e.g.*, below 0.5% by weight).

20 For example, U.S. Patent No. 4,586,995 ("the '995 patent") discloses "a novel
21 polymer and polymer treatment method . . . [which] involves irradiation of a polymer under
22 non-gelling conditions at a temperature above the polymer melting temperature and in the
23 absence of oxygen." See the '995 patent, abstract (emphasis added). The '995 patent,
24 therefore, teaches away from processes that irradiate polymers under gelling conditions
25 and/or at temperatures below the crystalline melt temperature and/or under unmodified
26 atmosphere.

27 As further example, U.S. Patent No. 6,114,486 ("the 486 patent") relates to "a
28 rheology-modified ethylene polymer having less than 0.5 weight percent gel . . . which is
29 characterized as having improved rheological performance and/or melt strength attributes
30 relative to the unmodified polymer." See the '486 patent abstract (emphasis added). "The
31 rheology . . . is modified . . . by treating the ethylene polymer in the presence of a

1 crosslinking agent in an amount . . . less than the amount which would cause more than 0.5
2 wt % gel formation . . . Crosslinking agents include peroxide compounds, and other known
3 heat-activated curing agents, such as azo compounds, and electron beam, gamma-ray, and
4 other known radiation cure systems.” Id. at col. 13 lines 10-20. When radiation is used,
5 “[t]he amount of energy used to modify the polymer is preferably at least 0.5 Mrad [5 kGy] .
6 . . and typically up to 50 Mrads [500 kGy].” Id. at col. 14 lines 9-12. “The irradiation
7 intensity is . . . adjusted to avoid substantial heating of the polymer, because that might
8 cause the polymer to react with oxygen . . . unless additional measures are taken to prevent
9 contact with oxygen.” Id. at col. 14 lines 18-25. The ‘486 patent, therefore, fails to
10 recognize any benefit of crosslinking polymers with radiation versus chemical crosslinking,
11 much less the benefits achieved using the irradiation conditions set forth herein, and also
12 teaches away from the modification of polymers to contain any significant amount of gel or
13 any significant reaction with oxygen.

14 In addition, European Patent Application No. 0047625 (“EPA ‘47625”) describes a
15 process whereby “[a] blend of polyethylene having a density in the range of 0.935-0.948
16 g/cm³ and 1-3%, by weight, of carbon black and which has been irradiated in an inert
17 atmosphere while in the form of granules, is fed to an extruder, extruded in the form of pipe
18 and cooled.” See EPA ‘47625 abstract (emphasis added). “In a preferred embodiment the
19 granules of polyethylene have been subjected to irradiation in an amount in the range of 0.05-
20 0.75 Mrad [0.5-7.5 kGy] of irradiation and particularly 0.3-0.7 [3-7 kGy] of irradiation.” Id.
21 at 4 lines 27-30. “Gel formation, on irradiation, in amounts of more than 0.1% by weight, is
22 outside the scope of this invention in the unlikely event that it should occur.” Id. at 5 lines
23 5-8. EPA ‘47625, therefore, teaches away from the irradiation of polyethylene under
24 ambient atmosphere, teaches away from the irradiation of polyethylene in the absence of
25 carbon black, teaches away from the generation of polyethylene with a gel content greater
26 than 0.1% by weight and, finally, fails to recognize the benefits achieved using the irradiation
27 conditions set forth herein.

28 Similarly, U.S. Patent No. 3,130,139 (the ‘139 patent”) describes a method whereby
29 “a uniform dispersion of carbon black in polyolefins is obtained by subjecting the polymer to
30 ionizing radiation prior to its admixture with the carbon black.” See the ‘139 patent col. 1
31 lines 41-45. “As little as 0.0005 megarad [0.005 kGy] . . . is effective to improve the

1 uniformity of dispersion of carbon black in polyolefins. As much as 10 megarads [100 kGy]
2 or more of ionizing radiations can be used for purposes of the present invention.” Id. at col.
3 2 lines 10-15. The ‘139 patent fails to recognize the benefits obtained from irradiating
4 polyethylene under the conditions set forth herein and, instead, utilizes a broad range of
5 doses to further the dispersion of a single filler, carbon black, that is neither required nor
6 preferred herein.

7 Finally, Great Britain Patent No. 831,896 (“GB ‘896”) “[r]elates to the production of
8 heat treated irradiated polymeric materials and blends of such materials with fillers.” See
9 GB ‘896 p. 1 lines 10-12. The method comprises “subjecting a polymer of at least one 1-
10 olefin . . . to a dosage of from 10^5 to 10^{11} roentgens [roughly 1 kGy to 1,000,000 kGy] of
11 radiation, and thereafter heating the irradiated polymer to a temperature above its softening
12 point.” Id. at p. 1 lines 49-59. “[T]he resulting product exhibits an increase in elongation
13 and a decrease in stiffness, density and tensile strength over that of either the un-irradiated or
14 irradiated starting polymer.” Id. at p.1 lines 19-24 (emphasis added). In the sole example,
15 “test specimens were placed in aluminum cans which were swept out with nitrogen and then
16 irradiated” Id. at p. 3 lines 112-115. GB ‘896 teaches away from the irradiation of
17 polyethylene under ambient atmosphere and teaches away from benefits, such as increased
18 tensile strength, obtained using the irradiation conditions described herein.

19 The inventors listed on this application have received prior patents relating to
20 polymer irradiation including the following: South African Patent No. 89/6852 (“S.A.
21 89/6852”) entitled “Crosslinking of Polymeric Materials;” South African Patent No. 92/6738
22 (“S.A. 92/6738”) entitled “Process For Coating A Substrate With A Film Of Thermoplastic
23 Polymeric Material; and South African Patent No. 98/9245 (“S.A. 98/9245”) entitled
24 “Crosslinking Of Polymeric Materials.” In general, these patents are directed toward the use
25 of multi-functional crosslinking agents in conjunction with irradiation. Furthermore, these
26 patents fail to recognize the revolutionary impact of carefully controlled irradiation on the
27 properties of polyethylene feedstock.

28 **3.0 SUMMARY OF THE INVENTION**

29 In the present invention, partial crosslinking, branching and oxidation in polyethylene
30 resins having a crystalline and an amorphous phase, prior to the formation of artifacts, is
31 induced using ionizing radiation at a temperature where both the crystalline and the

1 amorphous phases are present. Preferably, the irradiation is carried out in air and thus in the
2 presence of oxygen.

3 Irradiation under the conditions described herein induces a low degree crosslinking,
4 long chain branching and oxidation in the polymer. The irradiated polyethylene exhibits
5 enhanced mechanical properties – including thermal stability and improved processability.
6 For example, the irradiated polyethylene exhibits increased melt strength, tensile strength and
7 heat deflection temperature, decreased elongation at break, often exhibits improved notched
8 impact strength and, furthermore, possesses improved compatibility with other materials
9 (such as fillers) as well as improved adhesion to other materials (such as metal surfaces).
10 These benefits are achieved without destroying the ability to process and convert the
11 polyethylene into artifacts. Specifically, although the melt flow index of the polyethylene
12 drops with increasing dose, the irradiated polymer feedstock remains easy to process and
13 convert. Conversion of the irradiated polyethylene can be accomplished, optionally after
14 combination with additives, by a wide range of conversion technologies, *e.g.*, extrusion,
15 molding, film blowing and powder coating.

16 The degree of crosslinking within the polyethylene resin is controlled by radiation
17 dose, *i.e.*, energy absorbed by the irradiated polymer per unit mass (a common unit is kGy,
18 and 1 kGy = 1 kJ/kg). Ideally, the dose uniformity ratio (ratio of maximum dose to minimum
19 dose within the resin) ranges from 1.2 to 3.0 and, more preferably, ranges from 1.2 to 1.8.
20 The distribution of the dose within the material is also controlled.

21 While it is known to use radiation to impart a high degree of crosslinking (*e.g.*, 60-
22 70% gel content) to improve the material properties of formed parts, the method of this
23 invention achieves similar results using a much lower degree of crosslinking (*e.g.*, 0.01-8%
24 gel content) imparted prior to part formation. Preferably, the gel content ranges from 0.2 to
25 8%. More preferably, the gel content ranges from 0.75 to 8%. Ideally, the gel content ranges
26 from 0.75% to 6.0%. This is accomplished by applying low doses of radiation to the
27 polymer, *e.g.*, from 1 to 60 kGy, preferably from 8 to 30 kGy. In the case of electron beam,
28 these doses are surface doses. In the case of gamma ray and X-ray, these doses are the
29 minimum absorbed doses.

30 Preferably, the irradiation is conducted in an unmodified atmosphere and thus in the
31 presence of oxygen. It has been found that irradiation under these conditions imparts

1 superior compatability and adhesion properties to polyethylene. Thus, the modified
2 polyethylene can be more easily blended with polar additives and more easily adhered to
3 polar surfaces including metal (e.g., steel) surfaces, concrete, timber and polar plastics.

4 Electron beam, gamma ray and X-ray are all suitable forms of irradiation for use in
5 the invention. While gamma ray and X-ray have better penetration depth, electron beam
6 generally has higher dose rates which can lead to higher throughput, thus tending to be more
7 economical.

8 Other aspects of the invention will be apparent to those of ordinary skill in the art in
9 view of the disclosure provided herein.

10 **4.0 BRIEF DESCRIPTION OF THE DRAWINGS**

11 **FIG. 1** provides an energy deposition curve for a linear low density polyethylene
12 (LLDPE) with a density of 0.92 g/cm^3 irradiated using a 3 MeV electron beam accelerator.

13 **FIG. 2** illustrates the general impact of radiation induced crosslinking and long chain
14 branching on the melt flow index and spiral flow of polyethylene.

15 **FIG. 3** plots the weight-average molecular weight (M_w) of a irradiated high density
16 polyethylene (HDPE) versus surface dose.

17 **FIG. 4** plots the melt flow index of irradiated HDPE versus surface dose.

18 **FIG. 5** provides Large Amplitude Oscillatory Shear (LAOS) curves for irradiated and
19 un-irradiated HDPE.

20 **FIG. 6** illustrates a portion of a Fourier Transform Infrared Spectroscopy (FTIR)
21 spectra for an irradiated and un-irradiated HDPE.

22 **FIG. 7** plots the melt flow index of an irradiated LLDPE versus surface dose.

23 **5.0 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

24 **5.1 Definitions**

25 As used herein, the following terms are intended to have the following meaning:

26 "Homopolymer" refers to polymers prepared from one type of monomer.

27 "Copolymer" and "interpolymer" are used interchangeably to refer to polymers
28 prepared from two or more types of monomers.

29 "Ethylene polymer" and "Polyethylene" are used interchangeably to refer to polymers
30 that comprise at least 75% by weight units that are derived from ethylene and have the
31 structure $[-\text{CH}_2-\text{CH}_2-]_n$. Accordingly, the terms ethylene polymer and polyethylene include

1 ethylene homopolymers and ethylene copolymers. Preferably, any co-monomer present is an
2 α -olefin alkene such as 1-butene, 1-hexene, 1-octene and 4-methyl-1-pentene, however, the
3 presence of alternative co-monomers, especially vinyl acetate, is embraced.

4 "Branching" refers to the formation of shorter "Y-type" or "T-type" side chains
5 within a polymer structure that are attached to the longer backbone. In ethylene polymers,
6 branching is thought to be the result of the molecular addition of one polymer molecule to the
7 backbone of another polymer molecule.

8 "Oxidation" refers to the radiation-induced formation of functional groups such as
9 carboxylic groups via a peroxide radical mechanism in the presence and with the
10 involvement of oxygen.

11 "Short chain branching" refers to branches that consist of less than seven carbon
12 atoms. The term, therefore, includes methyl, ethyl, propyl, butyl, pentyl, and hexyl groups
13 that extend off the polymer backbone.

14 "Long chain branching" refers to branches that consist of seven or more carbon
15 atoms. The term, therefore, excludes methyl, ethyl, propyl, butyl, pentyl and hexyl groups
16 that extend of the polymer backbone.

17 "Low-density polyethylene" (LDPE) is an ethylene polymer that contains both short
18 and long chain branching. The presence of short and long chain branching interferes with the
19 formation of crystalline regions. Accordingly, LDPE has a relatively low degree of
20 crystallinity which is reflected by a low density. Generally, LDPE has a density under
21 ambient conditions ranging from 0.870 to 0.930 g/cm³. Polyethylenes with densities below
22 0.910 g/cm³ are sometimes referred to as very or ultra low density polyethylene (ULDPE or
23 ULDPE).

24 "Linear low density polyethylene" (LLDPE) is an ethylene polymer that contains
25 short chain branching and very little long chain branching. The term "linear" conveys the
26 absence of substantial long chain branching. LLDPE is made by polymerizing ethylene with
27 higher α -olefins. The use of a significant quantity of higher α -olefins (*e.g.*, > 1%) promotes
28 short chain branching. 1-Butene is a commonly employed α -olefin co-monomer for this
29 purpose. However, other co-monomers, such as 1-hexene, 1-octene, and 4-methyl-1-pentene
30 can be employed and provide enhanced physical properties at the expense of higher
31 production cost. The presence of short chain branching in LLDPE interferes with the ability

1 of the polymer to crystallize. Accordingly, LLDPE also has a relatively low degree of
2 crystallinity which is reflected by a low density. Generally, LLDPE has a density ranging
3 from 0.870 to 0.940 g/cm³.

4 "High-density polyethylene" (HDPE) is an ethylene polymer that is relatively free of
5 any kind of branching. The lack of branching permits the polymer to have a higher level of
6 crystallinity than LDPE and LLDPE which is reflected by a higher density. Generally,
7 HDPE has a density ranging from 0.945 to 0.970 g/cm³. Grades of HDPE that have a density
8 below 0.96 g/cm³ are produced using α -olefin co-monomer (e.g., 1-butene and 1-hexene) in
9 very low quantities (e.g., < 1%). The use of the second monomer reduces the density by
10 introducing short side chain branching. Such materials, which still exhibit less branching
11 than LDPE and LLDPE are often referred to as medium density polyethylene (MDPE).

12 "Crosslinking" refers to the formation of "H-type" chains in a polymer molecule,
13 where at least two polymer chains are bound together by one or more bridges formed by a
14 reacted element, group or compound. Increased crosslinking results in the formation of
15 increased amounts of gel. As used herein, no distinction is made between intermolecular
16 crosslinking and intramolecular crosslinking.

17 "Gel" refers to an insoluble three-dimensional polymer network formed by
18 crosslinking and/or branching. Gels are insoluble, even in solvents that dissolve the un-
19 crosslinked polymer.

20 "Gel fraction," also known as "gel content," is a measure of the amount of gel in a
21 polymer. Unless otherwise specified, gel fraction is determined by ASTM D-2765, the entire
22 content of which is incorporated by reference. Gel fraction is expressed in terms of weight
23 percent gel based on the total weight of the polymer.

24 "Number average molecular weight" (M_n) is one way of determining the molecular
25 weight of a polymer. The number average molecular weight is the common average of the
26 molecular weights of the individual polymers and is calculated in the conventional manner,
27 namely, measuring the molecular weight of a number (N) of polymer molecules, summing
28 the weights (M), and dividing by the total number of polymer molecules, i.e., $M_n = \sum N_i M_i / \sum N_i$. M_n is more sensitive to low molecular weight species than other measures of
29 molecular weight. Unless otherwise specified, M_n is measured by gel permeation
30 chromatography.
31

1 “Weight average molecular weight” (M_w) is another measure of the molecular weight
2 of a polymer. Weight average molecular weight is calculated in the conventional manner,
3 namely, by weighing a number (N) of polymer molecules, adding the squares of the weights
4 (M), and dividing by the total weight of the molecules, *i.e.*, $M_w = \sum N_i M_i^2 / \sum N_i M_i$. M_w is
5 more sensitive to higher molecular weight species than M_n . Unless otherwise specified, M_w
6 is measured by gel permeation chromatography.

7 “Molecular weight distribution” (MWD), also known as “molar mass distribution”
8 and “polydispersity,” is the uniformity of the chain length as calculated by the following
9 formula: M_w/M_n .

10 “Density” is a measure of mass per unit volume of material. Unless otherwise
11 specified, density is measured in accordance with ASTM D-1505, the entire content of which
12 is incorporated by reference.

13 “Melt flow index” (MFI), also known as melt index (MI) is the flow rate of
14 polyethylene under set conditions. The melt flow rate (MFR) is the ratio of two different
15 melt-flow indices using different loads in the determinations. Unless otherwise specified,
16 melt flow index is measured in accordance with ASTM D-1238 at 190°C and 2.16 kg load
17 (formerly known as Condition E), the entire content of which is incorporated by reference.

18 “Melt strength” is the tensile stress needed to break a polymer melt during draw
19 down. A high melt strength is needed for processes such as blow molding where the melt is
20 required to hold die shape and not sag after the melt leaves the die.

21 “Melt temperature” is the temperature of a material being melt processed.

22 “Tensile strength” is the maximum tensile stress that can be sustained by a material
23 under set conditions prior to a designated event (*e.g.*, yield or break). Unless otherwise
24 specified, tensile strength is measured in accordance with ISO 527, the entire content of
25 which is incorporated by reference.

26 “Elongation” is the degree of stretching, expressed as a percentage, that occurs under
27 set conditions at a designated point (*e.g.*, yield or break). Unless otherwise specified,
28 elongation is measured in accordance with ISO 527, the entire content of which is
29 incorporated by reference.

30 “Izod notched impact strength” is a measure of the impact resistance of a
31 thermoplastic as measured by a pendulum impact machine under set conditions. Unless

1 otherwise specified, Izod notched impact strength is measured in accordance with ISO 179,
2 the entire content of which is incorporated by reference.

3 “Shore D hardness” is a measure of hardness assessed by a material’s resistance to a
4 Type D indenter. Unless otherwise specified, shore D hardness is measured in accordance
5 with ISO 868, the entire content of which is incorporated by reference.

6 “Flexural strength,” also known as “flexural modulus” and “breaking strength,” is a
7 measure of the stiffness or rigidity of a material of given dimensions under a given load.
8 Unless otherwise specified, flexural strength is measured in accordance with ISO 527, the
9 entire content of which is incorporated by reference.

10 “Spiral Flow,” generally expressed in length, is a measure of the amount of material
11 that can be injection molded under set conditions prior to setting. Unless otherwise specified,
12 spiral flow is measured in according to ASTM D-3123, the entire content of which is
13 incorporated by reference.

14 “Service temperature” is the temperature at which a material can be used without
15 serious deterioration of properties such as loss of mechanical properties (and hence
16 deformation, etc.). Heat deflection temperature can be one indicator of service temperature.

17 “Heat deflection temperature” (HDT), also known as “heat distortion temperature,” is
18 the temperature at which a bar of polymer with given dimensions bends a given degree under
19 a given load. Unless otherwise specified, HDT is measured in accordance with ASTM D-
20 648, the entire content of which is incorporated by reference.

21 “Oxygen induction time” (OIT) is a measure of the ability of atmospheric oxygen to
22 degrade a polymer under set conditions (*e.g.*, elevated temperatures). OIT can be used as an
23 indirect measure of thermal stability. Unless otherwise specified, OIT is measured in
24 accordance with ASTM-3895, the entire content of which is incorporated by reference.

25 “Tear strength,” also known as tear resistance, is the force required to propagate a rip,
26 or tear, in a material, usually expressed as the ratio of the maximum load measured during
27 the test to the specimen thickness. Unless otherwise specified, tear strength is measured in
28 accordance with ASTM D-1922, the entire content of which is incorporated by reference.

29 “Hydrostatic stress strength” is the tensile stress at which a material fails when it is
30 formed into a pipe and subjected to hydrostatic internal pressure. Unless otherwise specified,

1 hydrostatic stress strength is measured in accordance with ISO 7628 Part 2, the entire content
2 of which is incorporated by reference.

3 "Unmodified atmosphere" means air. The word "unmodified" in this context conveys
4 that no steps are taken to modify the oxygen content of the air prior to irradiation. However,
5 because gases are consumed and/or released during irradiation induced crosslinking, the air
6 may or may not remain identical to normal air for the geographic region.

7 **5.2 Overview**

8 The invention focuses on the following four aspects for making radiation modified
9 resins for practical applications: (1) selection of the resin; (2) irradiation processing; (3)
10 formulation of the resin with additives; and (4) converting methods.

11 **5.3 Selection Of The Resin**

12 There are literally hundreds of commercially available grades of polyethylene that
13 can be employed in the present invention. Each grade varies in density, melt flow index,
14 molecular weight, molecular weight distribution, etc. In addition, polyethylene grades are
15 often created by different polymerization methods using different types and amounts of
16 catalysts and co-monomer. Most commercial grades contain additives (e.g., antioxidants,
17 processing aids, etc.) and the identity and quantity of these additives can vary.

18 Any commercially available ethylene polymer can be used in the present invention.
19 Preferably, however, the ethylene polymer employed has a density of at least 0.870 g/cm³
20 and a melt flow index at 190°C and 2.16 kg load of at least 0.1 g/10 min. By definition, the
21 ethylene polymer employed contains no more than 25% by weight units derived from non-
22 ethylenic co-monomers. Preferably, any co-monomer units present are polymerized α -olefin
23 units, although alternative unsaturated co-monomers, especially vinyl acetate, can also be
24 utilized. More preferably, any co-monomer utilized to polymerize the ethylene polymer is an
25 α -olefin alkene such as 1-butene, 1-hexene, 1-octene and 4-methyl-1-pentene. Ideally, any
26 co-monomer utilized contains no more than eight carbon atoms.

27 The polyethylene base resin is preferably manufactured using either a high- or a low-
28 pressure, or gas phase polymerization process. Such processes typically use chromium (Cr)
29 or titanium (Ti) based catalysts.

30 Criteria to be considered in selecting a polyethylene for radiation modification and
31 later use in a given process (e.g., extrusion, injection molding, film blowing, powder coating)

1 include density, melt flow index and mechanical properties, as well as the nature and
2 concentration of additives. In general, ethylene polymers that are preferred for a given
3 process in the absence of radiation modification remain preferred with radiation modification
4 since less radiation treatment is needed to optimize the performance of the resin.

5 If the polyethylene to be irradiated is intended for use in an extrusion process, HDPE
6 is a preferred selection. Preferably, in such instances, the HDPE has a density ranging from
7 0.945 to 0.970 g/cm³ and more preferably from 0.960 to 0.970 g/cm³. Preferably, in such
8 instances, the HDPE has a melt flow index at 190°C and 2.16 kg load that ranges from 0.1 to
9 2.0 g/10 min and more preferably from 0.1 to 0.2 g/10 min.

10 If the polyethylene to be irradiated is intended for use in a molding process (e.g.,
11 injection molding, blow molding, etc.), HDPE is again a preferred selection. Preferably, in
12 such instances, the HDPE has a density ranging from 0.945 to 0.970 g/cm³ and more
13 preferably from 0.950 to 0.965 g/cm³. Preferably, in such instances, the HDPE has a melt
14 flow index at 190 °C and 2.16 kg load that ranges from 0.5 to 20.0 g/10 min and more
15 preferably from 8.0 to 20.0 g/10 min.

16 If the polyethylene to be irradiated is intended for use in a film blowing process,
17 LLDPE is a preferred selection. Preferably, in such instances, the LLDPE has a density
18 ranging from 0.870 to 0.940 g/cm³ and more preferably from 0.910 to 0.925 g/cm³.
19 Preferably, in such instances, the LLDPE has a melt flow index at 190 °C and 2.16 kg load
20 that ranges from 0.4 to 10.0 g/10 min and more preferably from 0.7 to 1.2 g/10 min. The
21 LLDPE may, optionally, be blended with LDPE. However, one of the benefits of the
22 invention is that blends of LLDPE and LDPE are no longer necessary to achieve adequate
23 melt strength for the film blowing process.

24 If the polyethylene to be irradiated is intended for use in a powder coating process, a
25 blend of LLDPE and HDPE is a preferred selection. Preferably, in such instances, the
26 LLDPE has a density that ranges from 0.920 to 0.945 g/cm³ and more preferably from 0.930
27 to 0.945 g/cm³ and a melt flow index at 190 °C and 2.16 kg load that ranges from 2.0 to 10.0
28 g/10 min and more preferably from 3.5 to 5.0 g/10 min. Preferably, in such instances, the
29 HDPE has a density that ranges from 0.945 to 0.970 g/cm³ and more preferably from 0.950
30 to 0.965 g/cm³ and has a melt flow index at 190 °C and 2.16 kg load that ranges from 3.0 to
31 10.0 g/10 min and more preferably from 4.0 to 6.0 g/10 min. The ratio of LLDPE to HDPE

1 preferably ranges anywhere from 80:20 to 40:60 and more preferably ranges from 65:35 to
2 50:50.

3 Although additives may be present in the polyethylene, the polyethylene utilized
4 should contain little chemical crosslinking agent and, preferably, contains no chemical
5 crosslinking agent. In general, chemical crosslinking agents are only useful above the
6 crystalline melt temperature. As set forth later in this application, the irradiation process is
7 preferably conducted below the crystalline melt temperature. Accordingly, little benefit is
8 obtained from the presence of chemical crosslinking agents. Furthermore, the absence of
9 chemical crosslinking agents helps to ensure that articles made from the radiation crosslinked
10 material are fully recyclable and remain so over extended periods of time. The absence of
11 crosslinking agents also makes the polyethylene purer and suitable for food grades.

12 In addition, the polyethylene should contain as little antioxidant as possible.
13 Preferably, the concentration of any antioxidant present prior to irradiation is no more than
14 0.06% by weight of the polymer and, more preferably, is no more than 0.04% by weight of
15 the polymer. Radiation tends to deplete the level of any antioxidant present so high
16 concentrations of antioxidant are not particularly beneficial.

17 The polyethylene selected may be irradiated in any commercially available form.
18 Preferably, the polyethylene is in pellet or powdered form to facilitate continuous irradiation
19 processing.

20 **5.4 Irradiation Processing**

21 Radiation induces the formation of crosslinked networks in polyethylene. As a result,
22 the molecular weight of the polymer increases with increasing dose. In addition, the
23 molecular weight distribution widens, especially in cases where concurrent radiation induced
24 branching occurs. Gels are created. Gel fraction increases with increasing dose and is
25 indicative of an increasing degree of crosslinking.

26 Radiation induced crosslinking and branching enhances the mechanical properties of
27 the polyethylene including tensile strength and heat deflection temperature and generally
28 causes a decrease in elongation at break. In many cases, the notched impact strength
29 increases dramatically – but such increases are not evident in every case. The temperature
30 resistance, or thermal stability, is also improved. Heat deflection temperature, for example,

1 may be raised, indicating a higher service temperature. Other mechanical and physical
2 properties remain largely unchanged.

3 Radiation induced crosslinking and branching enhances the melt strength and
4 decreases the melt flow index of polyethylene. For applications such as film blowing, this is
5 especially important.

6 Radiation induced oxidation improves the compatibility of polyethylene to other
7 materials (such as fillers) and improves the adhesion of polyethylene to polar materials (such
8 as metal surfaces).

9 The degree of crosslinking within the polyethylene resin is controlled by radiation
10 dose, *i.e.*, energy absorbed by the irradiated polymer per unit mass (a common unit is kGy,
11 and 1 kGy = 1 kJ/kg). The distribution of the dose within the material is also controlled.

12 The required dose, and therefore the imparted degree of crosslinking, branching and
13 oxidation, varies depending on the nature of the resin, any additives therein, and its ultimate
14 intended application (*e.g.*, extrusion, molding, film or bottle blowing or powder coating).

15 Preferably, the crosslinking degree is relatively low. While it is known to use
16 radiation to impart a high degree of crosslinking (*e.g.*, 60-70% gel content) to formed parts in
17 order to significantly improve the material properties, the method of this invention achieves
18 similar results using a much lower degree of crosslinking (*e.g.*, 0.01-8% gel content)
19 imparted prior to part formation. The gel content preferably ranges 0.2 to 8 % by weight.
20 More preferably, the gel content ranges from 0.75 to 8 % by weight. Ideally, the gel content
21 ranges from 0.75% to 6.0 % by weight.

22 The requisite degree of crosslinking is accomplished by applying low doses or
23 radiation to the polymer. The specific minimum and maximum permissible absorbed dose is
24 determined by the choice of polymer and the specific additives in the polymer. Preferably,
25 the applied dose ranges from 1 to 60 kGy. More preferably, the applied dose ranges from 4
26 to 60 kGy. Even more preferably, the applied dose ranges between 8 and 50 kGy. Even
27 more preferably, the applied dose ranges from 8 to 30 kGy and, ideally, between 8 and 16
28 kGy. In the case of electron beam, these doses are surface doses. In the case of gamma ray
29 and X-ray, these doses are the minimum absorbed doses.

30 The dose uniformity ratio (ratio of maximum dose to the minimum dose within the
31 resin) is as uniform as possible. Typically, the dose uniformity ranges from 1.0 to 3.0, more

1 preferably from 1.0 to 2.0, and even more preferably from 1.0 to 1.8. A typical dos-
2 uniformity ratio is 1.30. When using electron beam, x-ray or gamma irradiation, the dose
3 uniformity ratio can be as near to 1.0 as desired, by selecting a thin layer of product. Of
4 course, this is at the expense of a lower throughput and loss of energy.

5 **FIG. 1** shows the energy deposition curve for a linear low density polyethylene
6 (LLDPE) with a density of 0.92 g/cm^3 irradiated using a 3 MeV electron beam accelerator.
7 The curve was generated by a computer simulation using the Monte Carlo Code ACCEPT of
8 the Integrated Tiger series Version 3 (3). The energy deposition is directly proportional to
9 the absorbed dose. **FIG. 1** shows that with the 3 MeV beam energy equal entrance absorbed
10 dose and exit absorbed dose can be achieved and a dose uniformity ratio of 1.45 can be
11 obtained at the penetration depth of 1.2 cm (not including air). The penetration depth will be
12 deeper if higher beam energy is used.

13 Preferably, irradiation is conducted at temperatures below the crystalline melt
14 temperature. More preferably, irradiation is conducted at a temperature between 10 and
15 80°C . Even more preferably, irradiation is conducted at ambient temperature - although the
16 temperature of the resin may increase during irradiation. If necessary, sufficient cooling can
17 be provided to maintain a resin temperature at or below 80°C .

18 The irradiation of polyethylene at a temperature below the crystalline melt
19 temperature imparts unique characteristics to the polyethylene that cannot be achieved using
20 chemically induced crosslinking or irradiation induced crosslinking at or above the
21 crystalline melt temperature. The unique results that are achieved are due to the
22 morphological characteristics of polyethylene. Below the crystalline melt temperature,
23 polyethylene has crystalline regions and amorphous regions. For chemical crosslinking, and
24 irradiation above the crystalline melt temperature, the crystalline regions are destroyed when
25 the polyethylene is heated above the crystalline melt temperature. In the melt phase, only
26 amorphous regions exist so any crosslinking is distributed homogeneously throughout the
27 resin. In contrast, when polyethylene is irradiated below the crystalline melt temperature, the
28 crystalline regions remain intact but any crosslinking remains predominantly localized in the
29 amorphous regions of the polymer with little crosslinking in the crystalline phase. This
30 causes a non-homogeneous crosslink distribution within the polymer.

1 Non-homogeneous crosslinking of polyethylene, predominately localized in the
 2 amorphous regions, only slightly impacts melt properties that are largely determined by
 3 crystalline regions. For example, while the melt flow index of polyethylene decreases
 4 sharply with increasing dose (even with low dose levels), the melt temperature and spiral
 5 flow (which is more indicative of flow behavior in converting processes) remain basically
 6 unchanged. Non-homogenous crosslinking of polyethylene, predominately localized in the
 7 amorphous regions, also permits the polyethylene to remain fully recyclable while,
 8 simultaneously, achieving the benefits of partial curing.

9 **FIG. 2** provides a schematic illustration of the impact of radiation induced
 10 crosslinking and branching, below the crystalline melt temperature, on polyethylene. **FIG. 2**
 11 shows a rapid decrease in melt flow index with an increasing dose. **FIG. 2** also shows a
 12 relatively stable spiral flow as the absorbed radiation dose increases. This is one of many
 13 features that are unique to the radiation modified polyethylene resins described herein.
 14 Namely, they maintain processability despite a decrease in melt flow index.

15 Table 1 provides a more specific illustration of the impact of radiation induced
 16 crosslinking and branching, below the crystalline melt temperature, on HDPE. The melt flow
 17 index was measured according to ASTM D-1238.

18 Table 1

Change In Melt Flow Index And Spiral Flow Of A Modified HDPE		
Absorbed Dose (kGy)	Melt flow index (g/10 min, 190°C, 21.6 kg)	Spiral Flow (cm)
8.0	5.0	26
16.0	3.5	26
24.0	1.8	24

19 As can be seen in Table 1, there is a marked decrease in the melt flow index with increasing
 20 radiation dose, but the spiral flow exhibits little corresponding change.

21 Preferably, irradiation is carried out in the presence of oxygen. More preferably,
 22 irradiation is carried out in an unmodified, and preferably uncontained, atmosphere. Ideally,
 23 the oxygen content in the chamber is at least 10%. Due to the release of gases during
 24 crosslinking, the atmosphere in the chamber may or may not remain identical to air that is
 25 normal for the geographic region. By performing the irradiation in the presence of oxygen,
 26 significant savings in equipment and processing costs are realized.

1 Equally as important, performing the irradiation in the presence of oxygen imparts
2 beneficial properties to the irradiated polyethylene resin. Oxygen in the air interacts in the
3 free radical mechanism of crosslinking. As a result, peroxide radicals are produced that
4 transform into functional groups, such as carboxylic (-COOH) groups, after subsequent
5 reactions. This radiation-induced oxidation favorably impacts the polymer's compatability
6 and adhesion with polar materials. For example, the introduction of functional groups such
7 as carboxylic groups increases the compatibility of polyethylene resin with polar additives,
8 making it easier to create homogeneous blends containing such additives. In addition, the
9 introduction of functional groups such as carboxylic acid increases the adhesion of the
10 polyethylene resin to other materials with polar characteristics. For applications such as
11 powder coatings, this means that the otherwise non-adhesive hydrophobic resin has natural
12 adhesion to polar metal substrates such as steel, as well as polar plastics.

13 Electron beam, gamma ray and X-ray are all suitable types of radiation for use in the
14 invention. The useful properties obtained by irradiating polyethylene at a given dose do not
15 vary in any significant degree with the type of ionizing radiation employed. While gamma
16 ray and X-ray have better penetration depth, electron beam generally has higher dose rates
17 which can lead to higher throughput, thus tending to be more economical. Where gamma
18 irradiators and X-ray are more suitable for treating the polymers in closed containers,
19 electron accelerators are more suitable to treating pelletized or powdered polymers in a
20 continuous manner.

21 Non-ionizing radiation is not suitable for use in the invention. For example,
22 ultraviolet radiation lacks sufficient material penetration capability.

23 Any known handling system may be employed in conjunction with the radiation
24 source. As known in the art, dose and dose uniformity can be determined, in part, by the
25 speed at which the samples pass through the irradiation chamber and by the orientation of the
26 samples relative to the radiation source. Suitable material handing systems include towlines,
27 tray conveyors, belt conveyors, cart conveyors and overhead chain conveyors, etc. Preferred
28 material handing systems are conveyors that transport trays of material and/or continuous
29 belt conveyors.

30

5.5 Formulation Of The Resin With Additives

Some additives may be present in the polyethylene resin, prior to irradiation, that are consumed by radicals produced during irradiation. Accordingly, additional additives can be incorporated into the polyethylene, after irradiation and prior to processing and conversion, to restore any beneficial properties derived from any depleted additives. Alternatively, additional additives can be added to the polyethylene resin, following irradiation and prior to processing and conversion, simply to incorporate additional beneficial properties not otherwise present. Illustrative additives that may be added after irradiation include pigments (colors), inorganic and organic fillers, antioxidants, UV stabilizers, heat stabilizers, processing aids, impact modifiers, antistatic agents, anti-slip agents, UV absorbers, etc. Preferably, antioxidants are the only additives added after irradiation since it is usually possible, using irradiation, to tailor the mechanical properties of the polyethylene as desired by varying dose.

Antioxidants are often added to the irradiated polyethylene resin to compensate for antioxidant consumed during the irradiation process. This helps to ensure that the long term thermal and oxygen stability of the polymer is not impaired by the irradiation process. For this purpose, any of the various commercially available antioxidants can be used. Preferred antioxidants include Irganox B-225 and Irganox B-900 from Ciba Specialty Chemicals.

Preferably, any additives mixed into the irradiated polyethylene resin are added in the form of a masterbatch, *i.e.*, high additive concentration compounded resins. For this purpose, either the base resin or the irradiated resin can be used to make the masterbatch. To make a masterbatch, a resin is mixed with a relatively high concentration of additive, extruded and pelletized. The total concentration of additives in the masterbatch can range anywhere from 0.1 to 20 weight percent, but preferably ranges from 2 to 5 weight percent. The irradiated resins are mechanically blended with the masterbatch to reach the final desired concentration of additives.

Preferably, the total concentration of additives in the irradiated polyethylene resin, after irradiation and additive addition, ranges from 0.01 to 0.5 weight percent. More preferably, the total concentration of additives in the final feedstock product ranges from 0.01 to 0.4 weight percent. Ideally, the total concentration of additives in the final feedstock product ranges from 0.05 to 0.2 wt%.

1 **5.6 Converting Methods**

2 Conventional converting equipment can be used to convert the irradiated
3 polyethylene resins with or without additional additives. However, it should be kept in mind
4 that radiation modification drastically decreases the melt flow index of the polyethylene.
5 Illustrative extrusion, injection molding, film blowing and powder coating processes, using
6 preferred irradiated polyethylene resins, are set forth below:

7 For extrusion processes, the preferred irradiated HDPE (with or without additives)
8 can be processed and converted using a conventional HDPE design screw. Care should be
9 taken to ensure sufficient motor power for processing. A temperature profile should be
10 chosen to ensure a melt temperature in the 220 °C to 255 °C range. The use of a hopper drier
11 is highly recommended. If needed, the surface finish of the extruded product can be
12 enhanced by increasing the temperature of the first section of the cooling bath to about 50 °C.

13 For injection molding processes, the preferred irradiated HDPE (with or without
14 additives) can be processed and converted using a conventional injection molder. Typical
15 processing conditions are as follows: a melt temperature that ranges from 220 °C to 240 °C;
16 an injection pressure (at the screw tip) up to machine maximum; a follow-up pressure (at the
17 screw tip) of 50 MPa maximum; an injection rate usually at the maximum depending on the
18 molding; a back pressure (at the screw tip) of 5 MPa to 30 MPa; a mold temperature ranging
19 from 20 °C to 40 °C; and a mold clamping force greater than 2500 N/cm² projected molding
20 area. However, the optimum molding conditions are dependent on a number of factors
21 including article flow length, mold gating, mold cooling facilities, etc.

22 For film blowing, the preferred irradiated LLDPE (with or without additives) can be
23 processed and converted to make a mono-layer film using conventional film blowing
24 equipment. Typical film blowing conditions include: a temperature profile where the
25 extruder is 190 °C, the neck is 190 °C, and the die is 190°C; a die gap of 3.0 to 3.2 mm,
26 preferably 3.1 mm (0.12"); and a blow-up ratio ranging from 2.4 to 2.5.

27 For powder coating, the preferred irradiated HDPE/LLDPE blend is compounded
28 with antioxidant and, optionally, other additives. The blend is then pulverized to make a
29 powder with a median particle size ranging from 20 to 600 microns, preferably from 70 to
30 400 microns. The powder is then coated onto a substrate, such as metal or plastic, using a

1 either fluidized bed, spraying or sintering processes. Preferably, the coating thickness ranges
2 from 0.1 to 5.0 mm and more preferably from 0.4 to 2.0 mm.

3 **5.7 Illustrative Products**

4 Irradiation of polyethylene under the conditions detailed herein enables the
5 production of a number of useful artifacts. The following is an illustrative list of artifacts:

6 **5.7.1 Extruded Pipes**

7 Pipes can be extruded from irradiated polyethylene. Pipes extruded from irradiated
8 HDPE exhibit a two-fold or greater increase in hydrostatic stress strength than pipes prepared
9 from conventional HDPE. The irradiation process enables the formation of pipes of
10 conventional wall thickness that can withstand higher internal pressures or, alternatively,
11 pipes with less than half the conventional wall thickness that can withstand equivalent
12 internal pressures. The latter pipes are less costly and easier to transport and handle than
13 conventional pipes. This enhancement of hydrostatic stress strength is even more
14 pronounced in the case of transporting fluids at elevated temperatures.

15 **5.7.2 Molded Products**

16 Molded products, such as injection molded luggage handles, clamps, and conveyor
17 parts, can be made from irradiated polyethylene. Irradiated HDPE, for example, is an
18 especially beneficial polyethylene for this purpose. Irradiated HDPE exhibits higher notched
19 impact resistance than conventional HDPE, as well as superior stiffness and wear properties.

20 **5.7.3 Extruded and/or Blown Films**

21 Films of irradiated polyethylene, especially irradiated LLDPE, can be prepared that
22 possess excellent puncture resistance as well as superior sealing strength. Unmodified
23 LLDPE grades provide very good film properties but cannot be blown into films due to poor
24 melt strength (*i.e.*, the melt flow index is too high). The conventional remedy has been to
25 blend LLDPE with LDPE, which has a much higher melt strength. The blend, typically
26 comprising about 75% LLDPE and about 25% LDPE by weight, exhibits greater melt
27 strength but only at the expense of film properties. Radiation induced crosslinking
28 sufficiently increases the melt strength of LLDPE so that blending with LDPE and
29 subsequent loss in film properties is no longer necessary (although it still may be desirable).

30 Specifically, un-irradiated LLDPE typically has a melt flow index ranging from 0.8 to
31 1.0 g/10 min. at 190°C and 2.16 kg load. By radiation crosslinking, this melt flow index can

typically be reduced to 0.3 to 0.5 g/10 min. at 190°C and 2.16 kg load. The low melt flow index of irradiated LLDPE permits extrusion and/or film blowing of a *mono film* or laminate for applications ranging from agricultural greenhouse sheeting, dam liners and general industrial films to those such as bags for transporting liquids. The irradiated LLDPE can be employed alone or in conjunction with LDPE (un-irradiated or irradiated).

More specifically, Table 2 compares the properties of films made from an irradiated LLDPE/LDPE blend to films made from an un-irradiated LLDPE/LDPE blend.

Table 2

Properties Of Films Formed From Un-Irradiated and Irradiated LLDPE/LDPE Starting Materials			
Film Property	Standard	Films Formed From Un-irradiated LLDPE/LDPE	Films Formed From Irradiated LLDPE/LDPE
Thickness (µm)	N/A	200	200
Tensile Strength, MD (MPa)	ISO 527	13.63	29.54
Tensile Strength, TD (MPa)	ISO 527	13.63	28.40
Elongation at Break, MD (%)	ISO 527	756.02	1458.84
Elongation at Break, TD (%)	ISO 527	968.27	1633.85
Tear Resistance, MD (N/mm)		114.10	155.00
Tear Resistance, TD (N/mm)		103.20	155.00

As evident from Table 2, films made from the irradiated materials exhibit more than twice the tensile strength and significantly enhanced tear resistance.

5.7.4 Powder Coatings

Irradiated polyethylene, especially, irradiated HDPE powder and blends thereof with LLDPE powder, exhibit excellent compatability and adhesion to metal (*e.g.*, steel) and other polar materials including polar plastics. This enhanced compatability and adhesion is due to the formation of polar groups on the polyethylene by irradiation. Adhesion strengths in excess of 6.5 N/mm are obtained as measured by South African Bureau of Standards (SABS) 1217-1984, entitled The Production of Painted And Powder-Coated Steel Pipes, the entirety of which is incorporated by reference. The modified polyethylene is, therefore, an excellent interior and exterior protective coating for metal structures including pipe, structural steel

1 and plastic surfaces. The increased compatability and adhesion means that the modified
2 polyethylene is also more easily used in multi-layer film and sheet extrusions – often
3 eliminating the need for intermediate adhesive layers. The polyethylene powders can be
4 applied by standard powder coating techniques.

5 **6.0 EXAMPLES**

6 **6.1 Example 1: Modified Resin For Injection Molding (Electron Beam)**

7 BP Solvay A60-70-162, an HDPE with a density of 0.963 g/cm^3 and a melt flow
8 index of 0.72 g/10 min ($2.16 \text{ kg/190 } ^\circ\text{C}$), was used as the non-modified polymer. The
9 polymerization of the resin involves a Cr-based loop slurry catalyst. The resin contains 500
10 ppm of phenolic antioxidant.

11 117 kg of A60-70-162 resin was irradiated with electron beam. The resin was
12 irradiated under ambient atmosphere and temperature in 18 aluminum trays with a dimension
13 of $16'' \times 14'' \times 12''$ (depth of each tray is $12''$). 6.50 kg of resin were evenly spread in each
14 tray. The electron beam accelerator utilized has an energy of 12 MeV and a beam power of 8
15 kW.

16 The surface dose was targeted at 8 kGy. Dose mapping was carried out using FWT
17 (Far West Technology Inc.) dosimeter films located on the top, at $1/3$ of the loading depth, at
18 $2/3$ of the loading depth and at the bottom, all located at the center of the tray. The surface
19 dose applied was determined to be 8.7 kGy. The dose uniformity ratio (ratio of maximum
20 dose to minimum dose) was determined to be 2.2. The average dose applied was calculated
21 to be 8.6 kGy.

22 Identical samples of A60-70-162 resin were irradiated by electron beam at other dose
23 levels, *i.e.*, surface dose of 16 kGy and 24 kGy. The weight-average molecular weight (M_w)
24 of all the samples were measured by GPC (Gel Permeation Chromatography).

25 **FIG. 3** plots the M_w of A60-70-162 versus surface does. As evident in **FIG. 3**, the
26 M_w increases with increasing surface radiation dose, indicating the occurrence of
27 crosslinking and probably branching. Although the first data point shows an initial decrease,
28 this is probably related to measurement uncertainty.

29 **FIG. 4** plots the melt flow index (MFI) of A60-70-162 at 190°C and under 10 kg load
30 versus dose level. As shown in **FIG. 4**, there is a drastic decrease of melt flow index with
31 increasing surface dose.

1 A masterbatch was prepared. Specifically, 117 kg of Dow's DMDA-8007 HDPE
 2 resin (with a density of 0.963 g/cm³ and a melt flow index of 8.0 g/10 min at 2.16 kg/190 °C)
 3 was irradiated with electron beam using the same irradiation method set forth above. 81 kg
 4 of the irradiated resin was then mixed with 2.77 kg Irganox B225 antioxidant from Ciba
 5 Specialty Chemicals, extruded and pelletized to make the masterbatch. Care was taken to
 6 ensure sufficient motor power for processing. A temperature profile was chosen to ensure a
 7 melt temperature in the 220 °C to 255 °C range.

8 50 kg of the irradiated A60-70-162 resin above was mixed with 1.5 kg of the
 9 masterbatch above using a 55 gallon drum and a drum roller to blend for 6 hours.

10 The above resin blend, as well as un-irradiated A60-70-162 (as control), were
 11 injection molded on an 80-ton Shinwa machine (with single-stage, single screw) to make
 12 dog-bone and flexural sample bars (1/8" or 3.2 mm thick). The barrel temperature was
 13 204°C and the mold coolant temperature was 71°C. Packing and cooling time combined was
 14 30 seconds per shot. The L/D ratio of the screw was approximately 20 to 1 and the
 15 compression ratio was approximately 2.5 to 1. The back pressure was low during the filling.
 16 Parts were filled using mold flow, primary injection pressure and injection speed as
 17 parameters. Secondary injection pressure was maintained until the gate froze and the part
 18 cooled enough to hold its integrity. The molder was purged several times before each run
 19 and a few extra sample bars were made with each run. Sample bars were successfully
 20 molded using both materials.

21 The sample bars were used to carry out tests for mechanical and thermal properties,
 22 etc. Table 3 shows the standards used and results obtained in the tests.

23 Table 3

Test Results For Electron Beam Modified Resin For Injection Molding				
Property	Unit	Standard	Un-irradiated A60-70-162	EB Irradiated A60-70-162
Melt Flow Index (190°C, 2.16 kg)	g/10min	ASTM D-1238	0.75	<0.10
Melt Flow Index (190°C, 10 kg)	g/10min	ASTM D-1238	10.7	1.1
Tensile Strength @ Yield ^[a]	MPa	ISO 527	29	39

Elongation @ Yield ^[a]	%	ISO 527	8	9
Tensile Strength @ Break ^[a]	MPa	ISO 527	13	21
Elongation @ Break ^[a]	%	ISO 527	106	20
Izod Notched Impact Strength	kJ/m ²	ISO 179	50*	54*
Heat Deflection Temperature (HDT, 66 psi)	°C	ASTM D-648	74	87
Oxygen Induction Time (OIT)	min.	ASTM D-3895	13.1	11.8

1 * Non-break failure, numerical numbers may be erroneous and are quoted for reference only
2 Table 3 shows that after electron beam irradiation, the melt flow index drastically decreased.
3 Some of the mechanical properties were improved. The heat deflection temperature (HDT)
4 was raised. The oxygen induction time (OIT) did not have much of a drop, indicating that
5 thermal stability did not deteriorate, probably due to the additional additives added through
6 the masterbatch.

7 **6.2 Example 2: Modified Resin For Injection Molding (Gamma Ray)**

8 Dow's DMDA-8007, an HDPE with a density of 0.963 g/cm³ and a melt flow index
9 of 8.0 g/10 min (2.16 kg/190 °C), was used as the non-modified polymer. The
10 polymerization of the resin involves a gas phase catalyst. The resin contains low
11 concentration of antioxidant.

12 100 kg of Dow's DMDA-8007 HDPE resin was irradiated with gamma ray. The
13 resin was irradiated under ambient atmosphere and temperature in 20 kg cardboard boxes,
14 each having the dimensions of 16" x 12.5" x 10". The 16" x 12.5" side was facing the
15 irradiator so that the depth that gamma ray penetrated was 10". There was no dead space
16 beyond the space among the pellets. The source activity was 2.2 MCi.

17 The minimum irradiation dose was targeted at 16 kGy. Dose mapping was carried
18 out using FWT dosimeter films. A total of 23 dosimeter films were placed on different
19 positions of the five 20 kg cartons and in the middle of the resin. The minimum dose was
20 determined to be 16.6 kGy and the dose uniformity ratio was 1.5. The average of all doses at
21 the 23 positions was calculated to be 21.4 kGy.

1 The number average molecular weight (M_n) and weight average molecular weight
2 (M_w) for both gamma irradiated DMDA 8007 and the unirradiated control were measured by
3 GPC. A GPC 2000V Waters instrument was used with a set of 3 columns (HT6E, HT6E,
4 HT2). The analysis was done at a temperature of 135°C in trichlorobenzene (TCB) and the
5 injection volume was 215.5 mL. The universal calibration was performed with 12 PS
6 standards, using the direct measured intrinsic viscosity with on-line viscometer. The
7 molecular weight obtained for broad samples was verified with PE NBS 1475 standard, as
8 the first and last sample in each sample set. Table 4 shows the M_n , M_w and the M_w/M_n
9 (polydispersity) values for both materials.

10 Table 4

Molecular Weight And Distribution For Gamma Radiation Modified Resin			
Sample	M_n (Daltons)	M_w (Daltons)	M_w/M_n
Un-Irradiated DMDA 8007	15600	103600	6.6
Irradiated DMDA 8007	14200	143200	10.1

11 Table 4 shows a significant increase of M_w/M_n after irradiation, which indicates a broadening
12 of molecular weight distribution as a result of long chain branching and crosslinking of the
13 polymer.

14 Large Amplitude Oscillatory Shear (LAOS) was measured for both gamma irradiated
15 DMDA 8007 and the unirradiated control. **FIG. 5** shows the shear stress vs. shear rate
16 curves for both materials at 190 °C. The broadening of the loop after irradiation indicates
17 that long chain branching has occurred after the radiation modification.

18 Fourier Transform Infrared (FTIR) spectroscopy for both gamma irradiated DMDA
19 8007 (16 kGy) and the un-irradiated control was taken. **FIG. 6** shows the carbonyl range of
20 the spectra. As illustrated by **FIG. 6**, new bands appear in the carbonyl range of the spectra
21 after gamma irradiation. The two bands located around 1741 cm^{-1} and 1716 cm^{-1} are
22 assigned to carbonyl stretching vibration in ester groups and in ketones respectively. The
23 small band that appears around 1698 cm^{-1} is assigned to the acid end-group. The changes
24 indicate that oxidation was induced by the irradiation and new carboxylic functional groups
25 were introduced onto the polyethylene.

Next, 39 kg of the gamma irradiated HDPE was mixed with 1.2 kg of the masterbatch from Example 1 above to form a blend. Blending was accomplished using a 55 gallon drum and a drum roller for 6 hours.

The above resin blend and the un-irradiated DMDA-8007 resin were, separately, injection molded on an 80-ton Shinwa machine (with single-stage, single screw) to make dog-bone and flexural sample bars (1/8" or 3.2 mm thick). The barrel temperature was 204°C and the mold coolant temperature was 71°C. Packing and cooling time combined was 30 seconds per shot. The L/D ratio of the screw is approximately 20 to 1 and the compression ratio is approximately 2.5 to 1. The back pressure was low during the filling. Parts were filled using mold flow, primary injection pressure and injection speed as parameters. Secondary injection pressure was maintained until the gate froze and the parts cooled enough to hold their integrity. The molder was purged several times before each running and a few extra sample bars were made with each running. Sample bars were successfully molded using both materials.

The sample bars were then used to carry out tests for mechanical and thermal properties, etc. Table 5 shows the standards used and results obtained in the tests.

Table 5

Test Results For Gamma Modified Resin For Injection Molding				
Property	Unit	Standard	Un-irradiated DMDA-8007	Gamma Irradiated DMDA-8007
Melt Flow Index (190°C, 2.16 kg)	g/10min	ASTM D-1238	8.6	1.1
Tensile Strength @ Yield ^[a]	MPa	ISO 527	28	30
Elongation @ Yield ^[a]	%	ISO 527	8	8
Tensile Strength @ Break ^[a]	MPa	ISO 527	No Break	15
Elongation @ Break ^[a]	%	ISO 527	>500	88
Izod Notched Impact Strength	kJ/m ²	ISO 179	6.1*	55*

Heat Deflection Temperature (HDT, 66 psi)	°C	ASTM D-648	73	83
Oxygen Induction Time (OIT)	min.	ASTM D-3895	3.6	5.9

1 * Non-break failure, numerical numbers may be erroneous and are quoted for reference only
2 Table 5 shows that after gamma irradiation, the melt flow index drastically decreased.
3 Mechanical properties were improved or remained the same. The heat deflection
4 temperature (HDT) rose. The oxygen induction time (OIT) was increased, indicating that
5 thermal stability was improved, probably due to additional additives added by the
6 masterbatch.

7 **6.3 Example 3: Modified Resin For Injection Molding (Gamma Ray)**

8 A HDPE (Dow's C7260) was irradiated to a minimum absorbed dose of 16 kGy using
9 gamma irradiation, employing bags containing 25 kg of polymer pellets. In addition, a
10 masterbatch with Irganox B225 additive was made using the irradiated HDPE and this
11 masterbatch was high-speed mixed into the irradiated polymer at a 3% masterbatch load.

12 The HDPE composition obtained exhibits a higher notched impact resistance than
13 conventional HDPE, as well as superior stiffness and wear properties. Due to its low melt
14 flow index, the irradiated HDPE composition is more suited to injection molding thicker
15 rather than thinner artifacts. For example, the irradiated HDPE composition is well suited for
16 injection molding luggage handles, clamps, and conveyor parts.

17 Various properties exhibited by the irradiated HDPE composition are set forth in
18 Table 6.

19 Table 6

Properties Exhibited By This Modified HDPE				
Property	Value	Unit	Test Method	Test Specimen
Density at 23 °C	>0.950	g/cm ³	ISO 1183	10 mm x 10 mm x 4 mm
Melt Flow Index		g/10 min	ISO 1183	granules
I ₅	16.0			
I ₂₁	3.5			
Spiral Flow Length	50 - 24	cm	1500 psi molding injection press	granules

Tensile at Yield	25 - 30	N/mm ²	ISO 527 Test rate 50 mm/min	ISO 3167, 4 mm thick
Tensile Strength	38	N/mm ²	ISO 527 Test rate 50 mm/min	ISO 3167, 4 mm thick
Flexural Modulus	17	N/mm ²	ISO 527 Test rate 50 mm/min	ISO 3167, 4 mm thick
Hardness Shore-D	66		ISO 868	ISO 3167, 4 mm thick
Notched Impact Strength at 23°C (acN)	4 - 50	kJ/m ²	ISO 179/1eA	80 mm x 10 mm x 4 mm

1 This irradiated HDPE composition can be processed on conventional injection
2 molders using the following processing conditions: (i) melt temperature between 220°C to
3 250°C; (ii) injection pressure (at the screw tip) up to the machine maximum; (iii) follow-up
4 pressure (at the screw tip) of 50 MPa maximum; (iv) injection rate usually maximum,
5 depending on the molding; (v) back pressure (at the screw tip) 5 MPa to 30 MPa; (vi) mold
6 temperature ranging from 20°C to 50°C; and (vii) mold clamping force greater than 2500
7 N/cm² projected molding area.

8 **6.4 Example 4: Modified Resin For Film Blowing (Electron Beam)**

9 Mono films made entirely from LLDPE offer good puncture and tear resistance
10 properties with superior environmental stress crack resistance (ESCR), but are difficult to
11 process since they cannot be produced with a melt flow index less than about 0.8. Therefore,
12 manufacturers use a mixture of 25% LDPE and 75% LLDPE in order to get satisfactory
13 processability at the expense of material properties. However, radiation modified LLDPE
14 offers the same or better processability and significantly improved tear resistance and
15 puncture resistance over those of materials currently used. The resulting material is well-
16 suited for thick film applications such as for greenhouses, dam liners, milk sachets and
17 various industrial applications.

18 Dow's Dowlex 2045G, a LLDPE with a density of 0.920 g/cm³ and a melt flow index
19 of 1.0 g/10 min (2.16 kg/190 °C) was used as the non-modified polymer.

20 96 kg of Dowlex 2045G resin was irradiated with electron beam. The surface dose
21 was targeted at 10 kGy. The resin was irradiated under ambient atmosphere and temperature

1 in 18 aluminum trays with the dimensions 16" x 14" x 12" (depth of each tray was 12") with
 2 5.34 kg resin evenly spread in each tray. The electron beam accelerator employed had an
 3 energy of 12 MeV and a beam power of 8 kW.

4 Dose mapping was carried out for a surface dose of 8 kGy using FWT dosimeter
 5 films on the top, at 1/3 of the loading depth, at 2/3 of the loading depth and at the bottom, all
 6 at the center of the tray. The surface dose was determined to be 8.4 kGy and the max./min.
 7 ratio was 1.2. The average dose was calculated to be 9.5 kGy.

8 Melt flow index (at 190 °C under 2.16 kg load) versus dose curves were obtained by
 9 irradiation of 5.34 kg Dowlex 2045G resin under the surface dose of 4, 8 and 16 kGy. FIG.
 10 7 shows the decrease in melt flow index with each increase in surface dose. The optimal
 11 surface dose was determined to be 10 kGy from the melt flow index versus surface dose
 12 curve, targeting a melt flow index of around 0.3 g/10min. after the irradiation.

13 The melt flow index at 190°C under 10 kg load (Condition N in ASTM D-1238) was
 14 also measured for the un-radiated control resin and the resin irradiated at 8 kGy. Table 7 lists
 15 the measured melt flow indices at 190°C under 2.16 kg and under 10 kg load, I_2 and I_{10} ,
 16 respectively, as well as the ratio of I_{10}/I_2 .

17 Table 7

Melt Flow Indices For Electron Beam Irradiated and Un-Irradiated LLDPE (Measured by ASTM D-1238, Condition N)			
Material	I_2	I_{10}	I_{10}/I_2
Dowlex 2045G Un-Irradiated	1.01	7.69	7.61
Dowlex 2045G EB Irradiated at 8 kGy	0.41	4.57	11.1

18 The ratio of I_{10}/I_2 increased after irradiation, indicating an increase in the degree of long
 19 chain branching. The benefits derived from increased long chain branching are partially
 20 discussed in U.S. Patent No. 6,114,486, the entire content of which is incorporated by
 21 reference.

22 To form a masterbatch, another 96 kg of Dow's Dowlex 2045G LLDPE resin was
 23 irradiated with an electron beam using the same irradiation method described above (at 10
 24 kGy surface dose). 81 kg of the irradiated resin was mixed with 2.77 kg Irganox B900
 25 antioxidant from Ciba Specialty Chemicals, extruded and pelletized to make the masterbatch.

1 Care was taken to ensure sufficient motor power for processing. A temperature profile was
2 chosen to ensure a melt temperature of about 190 °C.

3 50 kg of the irradiated Dowlex 2045G resin was mixed with 1.5 kg of the masterbatch
4 to form a blend. The blend was generated using a 55 gallon drum and a drum roller for 6
5 hours.

6 The above blend and the un-irradiated Dowlex 2045G resin (control) were used to
7 blow films. A 1.5" diameter single screw extruder was used for plasticating the resin. At the
8 end of the screw, a breaker plate with a 325-mesh screen was installed. A static mixer and a
9 4" diameter spiral mandrel die were installed inline with the extruder. The experimental
10 conditions utilized are presented in Table 8.

11 Table 8

Film Blowing Experimental Conditions		
Temperature	Zone 1	170 °F
	Zone 2	300 °F
	Zone 3	350 °F
	Zone 4	400 °F
	Die	450 °F
Screw Speed		20 rpm
Die Pressure		1800 psi
Line speed		25 ft/min to 150 ft/min
Film thickness		0.001 in. (25 µm) and 0.005 in. (127 µm)

12 The machine and the die were initially adjusted for a line speed of 25 ft/min. After
13 collecting samples, the line speed was progressively increased at a speed of 25 ft/min. The
14 bubble broke when the line speed was increased to 175 ft/min. 1 mil (25 µm) and 5 mil (127
15 µm) films of both resins were successfully produced.

16 The properties of 25 µm films made from both resins were examined. Table 9 lists
17 some of the results.

18 Table 9

Properties of (EB) Radiation Modified LLDPE			
Property	ASTM	Irradiated Dowlex 2045G with masterbatch	Dowlex 2045G unirradiated control
Tensile at yield (MPa) MD*	D 882	23.8	9.8

Tensile strength at break (MPa) MD	D 882	60.9	35.4
Elongation at break (%) MD	D 882	640	600
Tear strength (g/micron) MD	D 1004	13.2	7.0
Tensile at yield (MPa) TD*	D 882	18.8	8.2
Tensile breaking strength (MPa) TD	D 882	65.6	24.2
Elongation at break (%) TD	D 882	770	670
Tear strength (g/micron) TD	D 1004	15.4	7.7
Puncture Strength (gram)	D1306	581	481

1 * MD is machine direction, TD is transverse direction

2 Table 9 clearly indicates that the tensile strength, tear strength and puncture strength were
3 significantly increased after the radiation modification.

4 **6.5 Example 5: Modified Resins For Film Blowing (Gamma Ray)**

5 As stated in the preceding example, manufacturers previously mixed LLDPE with
6 LDPE to impart satisfactory processability at the expense of material properties. However,
7 irradiated LLDPE offers the same or better processability and exhibits much better tear
8 resistance and puncture resistance than those of material currently used.

9 An LLDPE (Sasol Polymers HF 12) was irradiated to a minimum absorbed dose of 8
10 kGy using gamma irradiation, employing bags containing 25 kg of polymer pellets. In
11 addition, a masterbatch with the appropriate additives was made using the irradiated LLDPE,
12 and this masterbatch was high-speed mixed into the irradiated polymer at a 3% masterbatch
13 load.

14 The low melt flow index of the irradiated LLDPE allows extrusion as a *mono film* or
15 laminate for applications ranging from agricultural greenhouse sheeting, dam liners and
16 general industrial films to those such as bags for transporting liquids. The film has excellent
17 puncture resistance as well as superior sealing strengths. Because of the superior melt
18 strength of the modified polymer, it results in a very stable blown film during extrusion.

19 The properties of the irradiated LLDPE film are set forth in Table 10.

20 Table 10

Properties of Radiation Modified LLDPE		
Property	ASTM Test	Measurements
Density at 23°C (g/cm ³)	D1505	0.922
Melt flow index (2.16kg/190°C) (g/10 min)	D1238	0.4
Tensile at yield (MPa) MD	D882	12.5

Tensile at yield (MPa) TD	D882	11.7
Tensile breaking strength (MPa) MD	D882	38.0
Tensile breaking strength (MPa) TD	D882	37.0
Elongation at break (%) MD	D882	>1 000
Elongation at break (%) TD	D882	>1 000
Tear strength (g/micron) MD	D1922	12.0
Tear strength (g/micron) TD	D1922	22.0
Impact resistance (F ₅₀ g)	D1709	>1200

6.6 Example 6: Modified Resins For Sheet Extrusion (Gamma Ray)

BP Solvay's K44-24-123, an HDPE with a density of 0.955 g/cm³ and a melt flow index of 21.0 g/10 min (21.6 kg/190 °C) was used as the non-modified polymer. 100 kg of K44-24-123 HDPE resin was irradiated with gamma ray. The resin was irradiated under ambient atmosphere and temperature in 20 kg cardboard boxes with the dimensions 16" x 12.5" x 10". The 16" x 12.5" side was facing the irradiator so that the depth that gamma ray penetrated was 10". There was no dead space beyond the space among the pellets. The source activity was 2.2 MCi.

The minimum irradiation dose was targeted at 16 kGy. Dose mapping was carried out using FWT dosimeter films. A total of 23 dosimeter films were placed on different positions of the five 20 kg cartons and in the middle of the resin. The minimum dose was determined to be 16.4 kGy and the dose uniformity ratio was 1.5. The average of all the doses at the 23 positions was calculated to be 22.0 kGy. The melt flow indices at 190 °C/10 kg were 24.0 g/10min. before the irradiation and 16.0 g/10min. after the irradiation.

39 kg of the above gamma irradiated HDPE was mixed with 1.2 kg of the masterbatch from Example 1 using a 55 gallon drum and a drum roller for 6 hours.

A Welex single screw extruder was used to extrude 40 mil (1 mm) thick sheet from the above resin blend and the un-irradiated K44-24-123 resin (as control). The extruder had a 1.24" barrel feeding a 10" width sheet die. The die temperature was 204°C. Sheets were successfully extruded using both materials, despite the decrease in melt flow index.

6.7 Example 7: Modified Resins For Pipe Extrusion (Gamma Ray)

Dow's M9255F, an HDPE with a density of 0.953 g/cm³ and a melt flow index of 8.5 g/10 min (21.6 kg/190 °C) was used as the non-modified polymer. The resin was irradiated under ambient atmosphere and temperature with gamma ray (source activity being 0.96 Mci)

1 in 25 kg bags. The minimum absorbed dose was 16 kGy with a dose uniformity ratio of
 2 1.30. Although the melt flow index decreased after irradiation, the spiral flow length
 3 exhibited little change (about 50 cm before and after irradiation).

4 The irradiated resin was subsequently compounded to add Irganox B225 antioxidant
 5 through a masterbatch using a similar method as described in Example 1 (the masterbatch
 6 was made from irradiated M9255F resin).

7 The modified and compounded polymer was used to extrude plumbing pipes with a
 8 12.8 mm outer diameter and a wall thickness of 1.9 mm. The pipes were tested according to
 9 *ISO 7628 Part 2* and South African standards SABS 1194: 1978, the entire contents of which
 10 are incorporated by reference. The test results are shown in Table 11.

11 Table 11

Test Results Of Pipes Made From Radiation Modified M9255F		
Property	Standardized Test	Result
Density at 23°C (g/cm ³)	ISO 1183	0.950
Melt flow index at 21.6 kg, 190°C (g/10 min)	ISO 1183	3.5
Spiral flow length (cm)		26
Tensile at yield (MPa)	ISO 527	30
Notched impact strength (kJ/m ²)	ISO 179eA	17
Pipe diameter (mm)		12.8
Pipe wall thickness (mm)		1.9
Burst test at 23 °C (MPa)	ISO 7628 (7.2)	9.74
Burst test at 100 °C (MPa)	ISO 7628 (7.2)	4.55
Hoop stress at 23 °C (MPa)		27.9
Hoop stress at 100 °C (MPa)		13.0
Tensile breaking strength (MPa)	SABS 1194: 1978	27.4
Elongation at break (%)	SABS 1194: 1978	506
Cold impact resistance (-40°C)	ISO 7628 (7.4)	No signs of cracking
Impact resistance (23 °C)	SABS 1194: 1978	No signs of cracking
Impact after ageing at 125 °C	ISO 7628 (7.5)	No signs of cracking
Moisture absorption at 100 °C	ISO 7628 (7.6)	<0.1%
Low temperature flexural at -40 °C (MPa)	ISO 7628 (7.7)	9.52
High temperature flexural at 100 °C (MPa)	ISO 7628 (7.8)	10.03
Stress cracking 60 °C (MPa)	ISO 7628 (7.9)	9.87
Resistance to ethanol (200 h)	ISO 7628 (7.10)	No signs of cracking
Resistance to battery acid (70 h)	ISO 7628 (7.11)	No signs of cracking

Resistance to oil (100 °C and 70 h) % change	ISO 7628 (7.12)	3.98
Burning rate (mm/min)	ISO 7628 (7.13)	19.91
Artificial weathering	SABS 1194: 1978	Stabilized for 5 years
Hardness (Shore D)	ISO 868	66

1 Table 11 shows that the hydrostatic stress strength, expressed as hoop stress, both at ambient
 2 temperature (23 °C) and at 100°C is much improved for the modified resin and, in fact, is at
 3 least double that of the non-modified polymer. This implies that the modification permits a
 4 pipe wall thickness reduction of up to one half that of the non-modified polymer, which has
 5 obvious safety and commercial advantages.

6 The hydrostatic stress strength (expressed as the hoop stress values) of the modified
 7 HDPE was compared to that of published values for pipes made from non-modified polymer
 8 as well as chemically crosslinked pipes. The results are shown below in Table 12 (all values
 9 in MPa).

10 Table 12

The Long-Term Hydrostatic Stress Strength (Hoop Stress) Of Radiation And Chemically Modified HDPEs			
Temperature (°C)	Non-Crosslinked HDPE	Chemically Crosslinked HDPE	Pre-Crosslinked HDPE*
23	12.4	12.5	17.4
80	5.5	6.0	
95		5.0	
100			8.1
110		3.5	

11 * Corrected by a safety factor of 1.6 for water pipes.

12 Table 12 shows that the hydrostatic stress strength of the radiation modified polymer not only
 13 surpasses that of the non-crosslinked polymer, but also surpasses that of chemically
 14 crosslinked polyethylene pipes (at ambient temperature by almost 40%). This enhancement
 15 is even more pronounced at 100 °C, with relative improvements in excess of 150%. The
 16 particular hydrostatic stress strength of the radiation-modified polyethylene is clearly
 17 demonstrated; especially at elevated operating temperatures.

18 Thus, the modified polyethylene enables the formation of pipes of conventional wall
 19 thickness that can withstand much higher internal pressures or, alternatively, pipes with half
 20 the conventional wall thickness that are able to withstand equivalent internal pressures. The

1 latter pipes are less costly and easier to transport and handle. This effect is even more
2 pronounced in the case of transporting fluids at elevated temperatures.

3 The spiral flow properties are essentially unchanged, which indicates little impact on
4 the ability to extrude the irradiated HDPE feedstock. Furthermore, the material is recyclable.

5 As an aside, it should be noted that the elevated melt strength of the modified
6 polyethylene also makes it amenable to blow molding applications where a shaped mass with
7 a much higher mass and strength can be manufactured. Accordingly, the material is ideally
8 suited for blow molding very large containers.

9 **6.8 Example 8: Modified Resins For Powder Coatings (Gamma Radiation)**

10 In general, polyethylene exhibits very poor bonding to steel and other metals as well
11 as other polar materials such as polar polymers. However, it has been discovered that polar
12 groups (*e.g.*, carboxylic acid groups) formed by irradiation impart polyethylene with
13 excellent compatability and adhesion to steel and other polar materials, in excess of 6.5
14 N/mm. This increased compatability and adhesion makes irradiated polyethylene an excellent
15 candidate for interior and exterior coating of steel pipes that carry water or food grade
16 materials, oil and gas pipes, structural steel, extruded profiles, and a number of other coating
17 applications. This increased compatability and adhesion also permits irradiated polyethylene
18 to be used in multi-layer film and sheet extrusions without intermediate adhesive layers.
19 Furthermore, it has been found that the irradiated polyethylene is easier to admix with polar
20 organic and inorganic additives.

21 In this vein, a thermoplastic powder coating system based on polyethylene was
22 developed for the protection of industrial steel structures and pipes. The polyethylene
23 utilized was an irradiated LLDPE/HDPE blend. The LLDPE utilized was Sasol Polymers
24 HR 411. The HDPE utilized was Dow C7260.

25 Specifically, a mixture of LLDPE (60%) and HDPE (40%) was compounded with an
26 appropriate masterbatch containing all the required additives (UV absorbers, antioxidants and
27 pigment) at a masterbatch concentration of 2.5% and palletized. The pellets were
28 subsequently milled to a powder with an average size of 600 microns and bagged in 25 kg
29 bags. The bagged powder was irradiated to a minimum absorbed dose of 16 kGy using
30 gamma radiation.

1 The irradiated LLDPE/HDPE obtained was applied to steel using standard powder
 2 coating techniques. Specifically, the irradiated LLDPE/HDPE blend was coated
 3 simultaneously inside and outside the steel pipes in a fluidized bed at steel surface
 4 temperatures of about 240 °C. No special pre-treatment of the steel was required and merely
 5 shot-blasting the steel to physically clean the surface rendered a coating with excellent
 6 adhesion and cathodic disbondment properties. Refurbishing old steel pipes can thus also be
 7 carried out employing this coating. The inherent abrasion resistance of the modified
 8 LLDPE/HDPE blend rendered a coating that was particularly well suited for protecting pipes
 9 transporting fluids containing abrasive particles, whereas the inherent inertness of
 10 polyethylene ensured an excellent protection against a chemically corrosive environment.
 11 The polymer and additives employed are classified as "food grades" and can be used in
 12 contact with potable water and foodstuffs. The powder coating imparted excellent corrosion
 13 and abrasion protection to the treated steel. Preliminary investigations reveal that similar
 14 protective coatings can be applied to other substrates including concrete and wood,
 15 employing flame spraying techniques.

16 Typical property values exhibited by irradiated LLDPE/HDPE steel pipe coatings
 17 made in this manner are set forth in Table 13.

18 Table 13

Property Values For Radiation Modified LLDPE/HDPE Steel Pipe Coatings			
Test	Standard	Units	Typical Value
Coating density		kg/m ³	>945
Thermal Stability		MFI change (%)	4.8
Adhesion to steel	SABS 1271-1984	N/mm	6.5
Adhesion to polyethylene		N/mm	21.2
Water absorption		% after 100 h	0
Penetration resistance		mm at 23°C	0.005
		mm at 70°C	0.102
Tensile at yield	ISO 527	MPa	21.2
ESCR*		F ₅₀ in hours	47
Impact resistance		J	20.4
Cathodic disbondment		Disbondment length (mm)	8.6

19 *a modified medium density can be used to improve this value.
 20

7.0 CONCLUDING REMARKS**7.1 Incorporation By Reference**

All documents, including all patents, standards and patent applications, mentioned in this specification are incorporated by reference to the same extent as if each document was specifically and individually indicated to be incorporated by reference. No admission is made that any document cited herein is prior art.

7.2 Spirit of the Invention

Although the invention has been fully described, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made without departing from the spirit the invention. Accordingly, the scope of the invention should be determined by the language of the claims and any equivalents thereof as defined by law.